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Lifetime lengthening through rotational coupling: Decay in the $^1B_{1g}$ and ^1A_u states of para-benzoquinone

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The lower excitations in the B_{1g} and A_u singlet states of para-benzoquinone correspond to the small molecule limit. Stern–Volmer type experiments in a supersonic jet have given the collision-free lifetimes of these states. These lifetimes increase with increasing rotation, which is due to the increased (Coriolis) coupling with the background manifold. Values for the vibronic and Coriolis coupling parameters can be extracted from the data. It then becomes evident that at about 2000 cm^{-1} above the origin the rotational effects are masked by the singlet–triplet radiationless decay, and indeed above that energy no rotational effects are observed.

INTRODUCTION

The dynamics of the singlet $n\pi^*$ states of *para*-benzoquinone (PBQ hereafter) are known to correspond to the small molecule limit. Experiments performed in bulk at room temperature showed that the singlet levels are intimately mixed with a sparse manifold of a lower electronic state.[1] A more detailed picture of the relaxation of PBQ was hindered by the extensive vibrational sequence congestion and rotational broadening in the room temperature spectrum.

We studied the time resolved emission of PBQ in a supersonic jet, where due to the extensive cooling of vibrational and rotational degrees of freedom a much more selective excitation is possible. We conclude from our data that the rotations play an important role in the radiationless processes in PBQ. In pyrazine, we found earlier[2] that increased rotation led to faster radiationless decay. In PBQ, increased rotation also leads to larger coupling, but, since it is in the small molecule limit, to slower decay.

THE LOWER $n\pi^*$ STATES OF PBQ

The electric dipole forbidden, magnetic dipole allowed origin of the $^1B_{1g} \leftarrow {}^1A_g$ transition is located at 20 045 cm^{-1}.[3] The transition is vibronically induced mainly through the activity of the $\nu_{22}(a_u)$ mode, resulting in a strong band at 20 978 cm^{-1}. We will further refer to this band as band E, according to Hollas.[4] A prominent ~ 1100 cm^{-1} progression is built upon band E, presumably arising from the totally symmetric C=O stretch vibration ν_2. The first member (band I) is observed at 22 040 cm^{-1}. A few very weak bands within 600 cm^{-1} from the $^1B_{1g}$ origin can be definitely assigned to the $^1A_u \leftarrow {}^1A_g$ transition whose origin is extrapolated at 19 991 cm^{-1}.[3] In the "hot" vapor absorption spectrum, they are completely obscured by the much stronger $^1B_{1g} \leftarrow {}^1A_g$ transition.[4]

With increasing energy, a diffuseness appears in the vapor absorption spectrum. This diffuseness up to 0.25 cm^{-1} may indicate strong coupling with another electronic state. From time resolved experiments on PBQ at room temperature, Brus and McDonald (BM)[1] concluded the radiative lifetime of the emitting levels to be two orders of magnitude longer than the pure radiative singlet lifetime.

EXPERIMENTAL

The pulsed nozzle used in our experiment was a modified Lucifer 121K04 magnetic valve with a 1 mm orifice. The minimum width of the gas pulses was about 4 ms with a rise time of about 0.5–1 ms. The coil was driven by 24 VDC pulses at a repetition rate of 20 Hz.

PBQ (vapor pressure 150 mTorr at room temperature)[1] was mixed with He and expanded at total pressures of up to 4 atm into a vacuum chamber. The vacuum chamber pressure was kept below 0.05 Torr by an Edwards 18B3A vapor booster pump (unbaffled pumping speed 1200 ℓ/s) backed by an Edwards ES 4000 mechanical pump. The beam was excited at an adjustable distance from the nozzle by the output of a Molectron DL 14P dye laser pumped by a UV 1000 nitrogen laser. Emission was collected by a 4× magnification telescope system and focused on an EMI 9558 photomultiplier filtered by a Corning filter 3-69. When appropriate, the emission was roughly dispersed by dielectric filters (bandpass 150 Å). The signal was fed into a PAR boxcar integrator to obtain excitation spectra or into single photon counting equipment already described elsewhere[5] for time-resolved experiments. A distance of only 1 cm along the beam axis is imaged homogeneously on the photomultiplier, a distance traveled by the beam in about 5 μs. This imposes a severe constraint on our time-resolved experiments, because some decays occur on a time scale up to 30 μs[1] and could therefore only be estimated.

COLLISIONS IN A JET

Simple continuum theory of an expanding gas in vacuum assumes thermal equilibrium throughout the expansion. The local temperature and density are then simply functions of the distance from the nozzle. A gradual transition from continuum flow to collisionless flow sets in when the internal degrees of freedom start to uncouple and the cooling is then governed by collision parameters instead of by thermodynamics. This transition region has recently been extensively discussed in a series of papers.[6,7]

The high instantaneous flow and the relatively large orifice diameter characteristic for a pulsed nozzle are very favorable for observing collisional effects on the fluorescent emission of large molecules admixed in a

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vanishing concentration in the expanding carrier gas. The continuum region is expected to extend over a few cm from the nozzle under our experimental conditions, and this region can be easily probed experimentally. Collisional effects on the emission of excited PBQ will be completely determined by the He–PBQ collision rate and, hence, by the local temperature and density of the expanding He jet downstream from the nozzle.

For a reversible isentropic adiabatic expansion of an ideal gas with specific heat ratio γ, the volume V and the pressure P obey the relation

$$PV^{\gamma} = \text{const.} \tag{1}$$

In a supersonic jet it is more convenient to consider the local density n and the local temperature T. At a point z on the beam axis one obtains with the ideal gas law from Relation (1)

$$n(z)/n_0 = (T(z)/T_0)^{[1/(\gamma-1)]} , \tag{2}$$

where the subscript zero denotes the stagnation value at $z = 0$. Considering the nozzle as a point source, the density of the "emitted" particles will fall as z^{-2} for sufficiently large z. From Relation (2), it can then be concluded that $T(z) \sim z^{-2(\gamma-1)}$. It is convenient to express z in terms of z_{ref}, which in its turn is a simple function of γ and the nozzle diameter D. Following the treatment of Habets,[7] the following expressions for $n(z)$ and $T(z)$ are obtained:

$$n(z) = n_0 (z/z_{\text{ref}})^{-2} , \tag{3}$$

$$T(z) = T_0 (z/z_{\text{ref}})^{-2(\gamma-1)} , \tag{4}$$

where the scaling parameter

$$z_{\text{ref}} = 0.71 \left[\left(\frac{2}{\gamma+1} \right)^{[1/(\gamma-1)]} \left(\frac{\gamma-1}{\gamma+1} \right)^{1/2} \right]^{1/2} D , \tag{5}$$

which yields $z_{\text{ref}} = 0.4D$ for a gas with $\gamma = 5/3$.

Taking σ for the fluorescence deactivation cross section for He–PBQ collisions, the effective collision frequency $Z(z)$ can be obtained as

$$Z(z) = \sigma n(z) \left[\frac{8kT(z)}{\pi\mu} \right]^{1/2} , \tag{6}$$

where μ is the reduced mass. The "zero pressure" fluorescence lifetime τ_0, the observed lifetime τ_{obs}, and the collision frequency $Z(z)$ are related by the Stern–Volmer relation. Using Eqs. (2)–(6) one obtains

$$\frac{1}{\tau_{\text{obs}}} = \frac{1}{\tau_0} + Z(z) = \frac{1}{\tau_0} + \sigma n_0 \left(\frac{8kT_0}{\mu\pi} \right)^{1/2} \left(\frac{z}{z_{\text{ref}}} \right)^{-8/3} . \tag{7}$$

Therefore, plotting $1/\tau_{\text{obs}}$ vs n_0 or vs $(z/z_{\text{ref}})^{-8/3}$ should yield straight lines with slopes containing σ and intercepts equal to $1/\tau_0$, the collision-free relaxation rate.

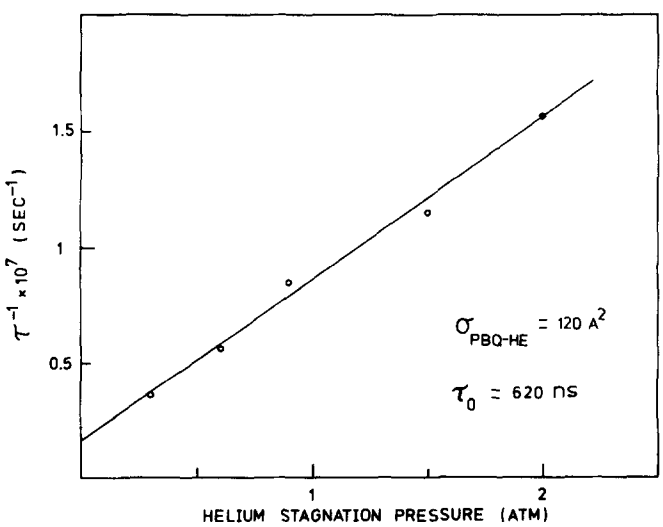

FIG. 1. Inverse fluorescence lifetime of band E as a function of the helium stagnation pressure. The cold PBQ molecules were excited at a distance of 1 cm from the 1 mm diameter nozzle.

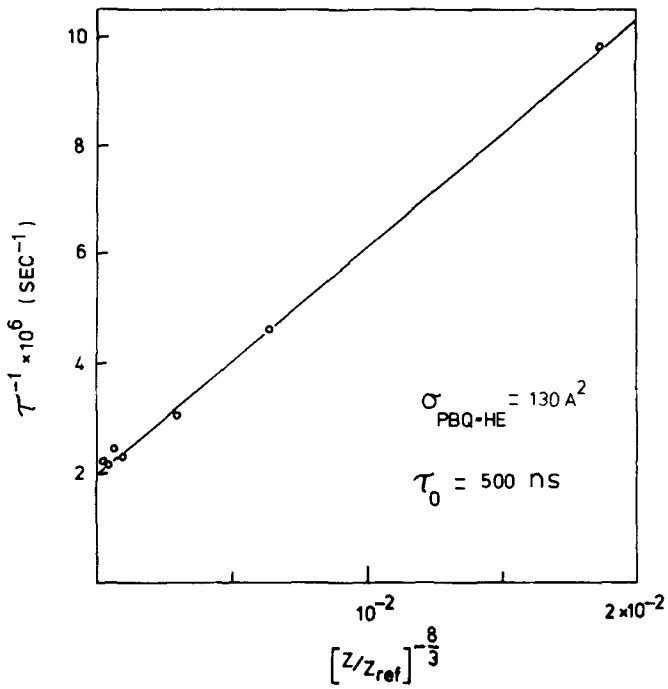

FIG. 2. Inverse fluorescence lifetime of band E as a function of the reduced distance from the nozzle. The stagnation pressure was kept at 1 atm.

RESULTS

In Fig. 1, we give a plot of the inverse fluorescence lifetime of PBQ excited in the E band at 20 978 cm^{-1} as a function of the stagnation pressure. The Stern–Volmer relation for a jet is very well obeyed. The effective collision cross section obtained from the slope is 120 Å^2 and the collision-free lifetime from the intercept is 620 ns.

A similar plot of $1/\tau_{\text{obs}}$ vs $(z/z_{\text{ref}})^{-8/3}$ is given in Fig. 2. Again, the Stern–Volmer analysis is vindicated; the values for σ and τ_0 are now 130 Å^2 and 500 ns, in good agreement with the above analysis. We feel that the latter values are the more reliable, since they are obtained closer to the "zero pressure" limit.

The fluorescence from band E was passed through a 5100 Å band pass filter which cuts off possible phos-

TABLE I. Collision-free lifetimes (± 10% accuracy) of single vibronic bands of PBQ-h_4.

Excess energy (cm^{-1})	Assignment	τ_0 (μs)	Remarks
0	$^1B_{1g}$ (0,0)	0.26	
125	26_0^1	0.36	
322[a]	30_0^1	0.42	
383	23_0^1	0.29	
654	25_0^1	0.36	
933	22_0^1	0.50	band *E*
1367	$22_0^1 6_0^1$	1.40	
1998	$22_0^1 2_0^1$?	> 5[b]	band *I*
2436	$22_0^1 2_0^1 6_0^1$	> 5[b]	

[a]Excess energy with respect to the ^1A_u electronic origin at 19991 cm^{-1}.
[b]Lifetime uncertain but more than 5 μs.

phorescence induced by residual collisions with background molecules. It should be noted that the path traveled by the molecules in 500 ns (~ 1 mm) is short enough to assure that the collision number $Z(z)$ is constant if the laser beam is focused well enough.

Fluorescence lifetimes of other singlet vibronic levels were measured after excitation at 6 cm from the nozzle and at a stagnation pressure of 2 atm. They can be considered as collision-free assuming that their cross sections for fluorescence quenching do not exceed the value of 130 Å^2. The results are listed in Table I. Lifetimes of vibronic bands with energies up to 1000 cm^{-1} are exponential up to about 2 *e* decades and followed by a much slower nonexponential looking emission, to which, if exponential at all, can be accorded a lifetime of more than 5 μs. We will return to this point later.

We can conclude that at low excess energy ($E_{exc} \lesssim 1500$ cm^{-1}) in the first excited singlet states of PBQ, the vibronic bands have collision-free lifetimes of 250–1500 ns.

On the other hand, states at higher excess energies ($E_{exc} > 1500$ cm^{-1}), such as band *I* have much longer lifetimes; we estimate about 10 μs, although we cannot really measure them in our apparatus.

COLLISION INDUCED INTERSYSTEM CROSSING IN PBQ

BM showed that in PBQ the collisional fluorescence quenching is partially, if not completely, responsible for the induction of phosphorescence from the ^3A_u state with the origin located at 18682 cm^{-1}. Indeed, we observe that in the presence of collisions, the fluorescence from band *E* is accompanied by a "long-lived" phosphorescence. At $t = 0$, the amplitude of the fluorescence is about ten times larger than the amplitude of the collision induced phosphorence at the maximum collision number attainable with our present experimental setup. When the emission originating from band *E* is recorded at higher resolution (10 Å) (see Fig. 3), the spectrum shows under collision-free conditions weak bands which are identified as 2_1^0 (and/or 3_1^0), 5_1^0, and 6_1^0 of a_g fundamentals also active in the $^1B_{1g} \leftarrow {}^1A_g$ absorption spectrum. The strongest feature is attributed to 22_2^0, the a_u mode excited. Closer to the nozzle, we see the phosphorescence grow in, peaking around 18680 cm^{-1}, where indeed the ^3A_u origin is located, and around 17000 cm^{-1}, which is assigned as 2_1^0 and/or 3_1^0, also active in the triplet absorption spectrum.[8,9] The much weaker bands below band *E* show a similar phosphorescence induction. The collisional fluorescence deactivation rate of the fluorescence from band *I*, however, is much slower. No effects on the lifetime are observed under similar expansion conditions as for band *E*, although some phosphorescence induction is observed when the emission is crudely dispersed by narrow bandpass filters.

BM also measured the fluorescence deactivation rate for PBQ–PBQ collisions and found no dependence on excitation energy. The same holds probably for the deactivation cross section for PBQ–Ar collisions which they measured only for band *I*. The cross section of 3–4 Å^2 they obtained for Ar–PBQ may be considered as an upper limit for He–PBQ collisions. However, for band *E* we find a cross section which is at least more than an order of magnitude larger.

The data of BM thus differ from ours in two aspects: (a) They find essentially constant lifetimes, everywhere in the singlet manifold, while we find (Table I) that they increase steadily in the range $0 < E_{exc} < 2000$ cm^{-1}. (b) They find no dependence of the collisional cross section for intersystem crossing on the excess energy, while we

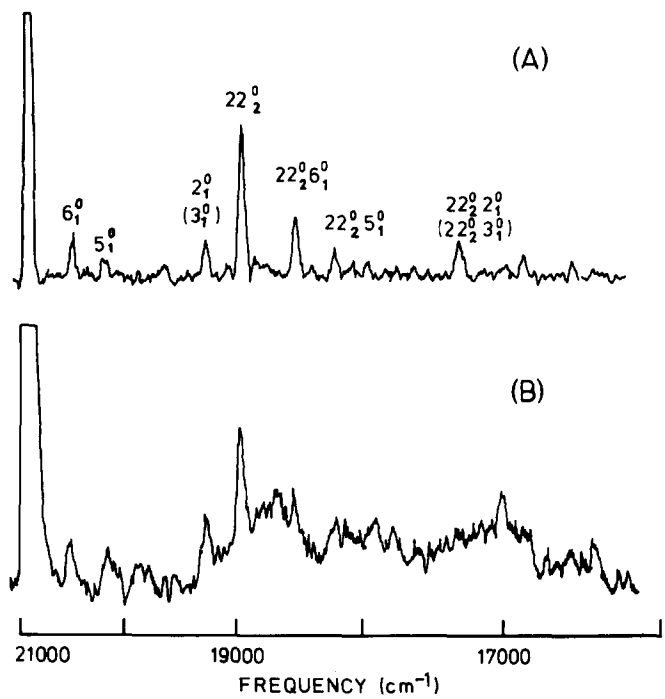

FIG. 3. (A) Fluorescence spectrum of PBQ excited in band *E* under collision-free conditions. (B) Fluorescence and thermalized phosphorescence spectrum after excitation close to the nozzle. In both cases, the instrumental spectral width is 10 Å. It is clear that the integrated phosphorescence intensity is much larger than the integrated fluorescence intensity.

find its value to decrease from about 100 Å^2 at $E_{exc}=0$ to about 3 Å^2 at $E_{exc}\simeq 2000$ cm^{-1}. We could with our equipment roughly substantiate the data of BM as well; the difference is therefore not of an experimental nature.

In the next paragraph we show that this difference is due to the difference in rotational population.

ROTATIONAL DEPENDENCE OF THE DYNAMICS OF PBQ

So far we discussed SVL lifetimes of really "cold" molecules, i.e., molecules with a rotational temperature of 1–2 K. Therefore, so far our results are only pertinent to molecules in their first few rotational states.

By manipulating the source pressure we could, however, increase the rotational temperature to about 15 K, and for band E we were, with a resolution of 0.5 cm^{-1}, able to measure lifetimes of rotational states, which have their absorption further away from the 0–0 frequency. We find that over the rotational contour the lifetimes vary by about a factor of 4.

Unfortunately, the ground and excited state rotational constants of PBQ are such[10] that no rotational structure can be resolved, even with the best resolution we can obtain (≈ 0.1 cm^{-1}). The effect is, however, immediately obvious from Fig. 4, where we compare the fluorescence excitation spectrum of the rotational contour of the E band with the detection window of the boxcar (30 ns) set at 50 ns with the same spectrum obtained with the detection window at a much later time (2 μs). It

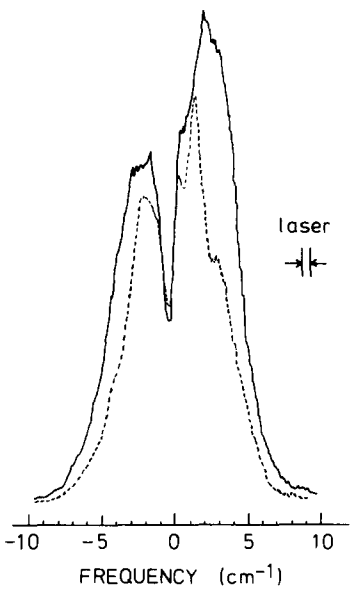

FIG. 4. Fluorescence excitation spectra of the E band at 20 978 cm^{-1} with the 30 ns detection window set at 2 μs delay (solid line) and at zero delay (broken line). The "delayed" excitation spectrum shows relatively more intensity in the wings or at high rotational quantum numbers, qualitatively indicating an increasing lifetime with increasing rotational excitation. Note that because of this effect the "delayed" spectrum appears broader. PBQ was excited at 2 cm from the 1 mm diameter nozzle at a helium stagnation pressure of 200 Torr. The rotational temperature is estimated as 15 ± 5 K.

is clear that the wings of the contour (high J's) decay much slower than the center.

Probably, because we always excite "packets" of J, K states, the decays are nonexponential. If we, nevertheless, define half the value of time in which the decay proceeds to $1/e^2$ of its initial amplitude, then we find at $J\approx 0$ a "lifetime" of 1.4 μs and at $J\approx 15$ about 2 μs.

We conclude that the lifetime of the state increases steadily with J. Now the apparent contradiction between the data of BM and us is resolved. At room temperature one measures an average over high J values, and much longer decay times, in the order of 7–15 μs, can then be expected.

It can now be understood why the collision-free lifetimes of cold bands with excess energies up to 1000 cm^{-1} are slightly nonexponential on a time scale longer than 1 μs. We tentatively attribute this long living background to fluorescence from higher rotational states. The possibility, however, that this long living emission is actually residual phosphorescence cannot be excluded, considering the high sensitivity for collisions in this energy region.

DISCUSSION

An explanation of our data has to account for the following observations: (1) the drastic increase in lifetime of the vibronic states of the cold isolated molecule as a function of excess excitation energy up to 2000 cm^{-1} and (2) the increase in lifetime as a function of rotational quantum number, as observed in band E.

If the molecules excited in the rovibronic $^1B_{1g}$ levels were quenched into the ^3A_u triplet with unity efficiency, then the minimal intensity ratio of the fluorescence and the collision induced phosphorescence at $t=0$ would be the ratio between the pure radiative rates, i.e., about 100. We recall that the observed ratio is at most 10, which means that the absorbing levels have a radiative rate lower by a factor of 10 and therefore are not pure singlet levels but mixed states due to strong coupling of the singlet levels with a lower electronic state. The ^3A_u state whose vibronic manifold is sparse at the energy of interest is the most likely state to be involved in the mixing. We distinguish two cases:

(A) The vibrational singlet levels are coupled vibronically to the triplet state. This case can be treated in the standard way.[11] The number N_v of levels effectively coupled vibronically to the singlet can be expressed as $N_v=2\pi^2\nu_{ST}^2\rho_T^2$, where ν_{ST} is the coupling matrix element and ρ_T the triplet vibrational density.

(B) The rovibrational singlet levels are coupled to rotational triplet levels by, for instance, Coriolis coupling. In first order we may consider this coupling independent of the vibronic coupling. This case is more problematic from a theoretical point of view. Thus far, only few theoretical treatments of the rotational effects on radiationless transitions have been published. Recently, Novak and Rice took into account the effect of Coriolis coupling on the internal conversion and intersystem crossing rate and derived an explicit K^2 dependence.[12,13] Brand and Stevens[14,15] considered the intersystem spin–

rotation coupling and derived an expression dependent on both J and K. Considering these theoretical treatments, we suggest the following analysis. The number of levels interacting with a rovibronic singlet we take as: $N_K = 2\pi^2 \nu_K^2 \rho_K^2$, where ν_K is a rotationally dependent matrix element and ρ_K the triplet rovibronic level density. The rovibrational singlet will couple with a number of rovibrational triplets with their J and K in the neighborhood of the J and K of the singlet. Together with the threefoldness of the triplet, the effective density may well be about a factor of 10 higher than the vibrational density ρ_T, as calculated by the Haarhoff formulas.[16] We take $\rho_K \simeq 10\rho_T$. Assuming further that ν_K can be expressed as $\nu_K = aK$, where K is one of the rotational quantum numbers, we obtain for the number of rovibronic triplet levels coupled $N_K = 2\pi^2(ak)^2(10\rho_T)^2$, and thus for the total number of coupled levels $N = 2\pi^2 \rho_T^2 [\nu_{ST}^2 + (10aK)^2]$. When the Maxwell–Boltzmann averaged quantum number K is about 3 in the cold jet, we derive $N \simeq 10$ from the relative intensity ratio of the fluorescence and collision induced phosphorescence. Similarly, we observe a lifetime lengthening of a factor of 4 at a rotational temperature where the average K is about 15. Thus, for $K \simeq 15$, $N \simeq 40$. Further, the triplet level density ρ_T at 1000 cm^{-1} singlet excess energy (E band) is calculated to be $\rho_T \simeq 28$ cm from the Haarhoff formulas. From these data ν_{ST} and a can be rougly estimated to be 2.4×10^{-2} cm^{-1} and 3×10^{-4} cm^{-1}, respectively. We emphasize that the numbers obtained are only indicative because of the theoretical uncertainties. Also, a detailed rotational analysis is impossible with our present equipment.

Having now found a simple way to include rotational effects on the lifetime, we are also in a position to account for the further nonradiative behavior of the rovibronic state of PBQ.

In the small molecule limit, we have for the decay rate of the rovibronic $S-T$ mixed state M

$$\gamma_M = \gamma_S/N + \gamma_T \quad ,$$

where $\gamma_S = \Gamma_S^{rad} + \gamma_S^{nrad}$, the total decay rate of the singlet, and $\gamma_T = \Gamma_T^{rad} + \gamma_T^{nrad}$, the decay rate of the set of triplet states. With γ_M as observed 2×10^6 s^{-1}, $\Gamma_T = 8\times10^2$ s^{-1}, $\gamma_T^{nrad} = 3.5\times10^4$ s^{-1}, $\Gamma_S^{rad} = 8\times10^4$ s^{-1}, and (for $K \approx 0$) $N = 10$ for band E, it follows that we have $\gamma_S^{nrad} = 2\times10^7$ s^{-1} for the singlet state mixed into this molecular eigenstate. As the excess energy increases, ρ_T increases and thus N. This effect is responsible for the lifetime lengthening observed as a function of excess energy. At $E_{exc} \simeq 2000$ cm^{-1}, the I band, a Haarhoff estimate for ρ_T is about 700 cm. Taking the matrix element ν_{ST} the same, then $N \simeq 6250$ even at $K = 0$. Thus, $\gamma_M = \gamma_S/N + \gamma_T$ then yields $\gamma_M \approx \gamma_T$, the behavior of the molecular eigenstates being completely governed by that of the triplet states. This is also true for large K values at lower energies, such as obtained in the "hot" vapor phase experiments of Brus and McDonald. At $E_{exc} \simeq 1000$ cm^{-1} (E band), we find from their experiments $\gamma_T \simeq 6.7\times10^4$ s^{-1}, at $E_{excess} \simeq 2000$ cm^{-1} (I band) $\gamma_T \simeq 10^5$ s^{-1}, while in the thermal triplet $\gamma_T \simeq 3.5\times10^4$ s^{-1}. Apparently, the radiationless rate of the triplet state slowly increases with energy.

Therefore, the increase of ρ_T with energy is responsible for the increase of lifetime with energy, while the increase of the matrix element with K is responsible for the lifetime lengthening as a function of rotation at low excess energies. The lifetime "bottoms out" in both cases when the triplet lifetime is reached. The rotational effects are then, of course, completely masked.

Finally, we have to account for the dramatic change of σ with energy or K. It would seem that we have here a situation comparable to biacetyl.[5] If E_{exc} and K are low, only very few states ($N \simeq 10$) of the triplet manifold have a singlet component and they spread over a very small energy range, about 0.1 cm^{-1}, comparable to a typical rotational spacing. Therefore, the molecular eigenstate manifold has regions with "light" (singlet containing) and "dark" (pure triplet) character, i.e., "black holes."[5] This may be so for the lower energy E band; but for the I band with $\rho_T \simeq 700$ cm, the spread of energy becomes about 3 cm^{-1}, which is larger than the singlet rotational spacing, and therefore the whole molecular eigenstate manifold now has singlet character, i.e., there are no "black holes."

In a jet, the typical collision energies are low and the effective collision cross sections are then usually high.[17–19] In the low energy E band, it takes very little energy to transfer a PBQ molecule into a black hole and in accordance with this we find a large cross section for fluorescence quenching. For the high energy I band, there are no black holes and it takes large amounts of energy to quench the fluorescence. The cross section for this process is then low. At high temperatures, such as in the BM experiments, either the high energy collisions are "überhaupt" less efficient or the spread of the coupled rotational triplet levels which goes as K^2 has increased so much for the room temperature average K's of about 40 that no black holes are left.

CONCLUSIONS

We can conclude that the dynamics of the states in PBQ follow the small molecule regime. The states are intimately mixed with the triplet background. The number of admixed states increases with rotation because the matrix element for the coupling is a function of the square of the rotational quantum number K. In contrast to the case of pyrazine in which this mechanism leads to lifetime shortening, it leads to lifetime lengthening in PBQ because we start in the small molecule limit. This effect is absent at higher vibrational energies, since the triplet background vibrational density becomes much higher and the rotational effect is masked.

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